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(54) Title: DURABLY WETTABLE, LIQUID PERVIOUS WEBS		
(57) Abstract Disclosed are durably wettable, liquid pervious webs that are particularly useful as topsheet materials for absorbent articles, such as baby and adult diapers, feminine hygiene products and the like. The durably wettable, liquid pervious webs are formed by applying a relatively permanent hydrophilic coating onto at least one surface of a web (a polymeric film or nonwoven) via plasma polymerization. Also disclosed are absorbent articles which include the durably wettable, liquid pervious webs as a topsheet, as well as the plasma polymerization process for making the durably wettable, liquid pervious webs.		

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DURABLY WETTABLE, LIQUID PERVIOUS WEBS

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CROSS REFERENCE TO RELATED APPLICATIONS

This is a Continuation-in-Part of co-pending application Serial No. 09/157,845 filed September 29, 1998.

TECHNICAL FIELD

10 The present invention relates to a durably wettable, liquid pervious web that is particularly suitable as a topsheet for absorbent articles. More particularly, the invention relates to a polymeric film or nonwoven to which is applied a thin coating of organic material onto at least one surface of the film or nonwoven. The thin organic coating is applied by a plasma-induced chemical vapor deposition process. The thin organic coating renders the web more permanently hydrophilic than other methods known in the art. The invention further relates to a process for making the durably wettable, liquid pervious web, and to articles containing the durably wettable, liquid pervious web as a topsheet.

BACKGROUND OF THE INVENTION

20 Polymeric and nonwoven webs are common components of disposable absorbant articles, dryer sheets and the like. More particularly, macroscopically expanded, three-dimensional, polymeric films have been utilized as topsheet materials for disposable absorbent articles. As used herein, the term "macroscopically expanded", when used to describe three-dimensional webs, refers to webs which have been caused to conform to the surface of a three-dimensional forming structure so that both surfaces thereof exhibit the three-dimensional pattern of the forming structure or webs that have an inherent three-dimensional pattern arising from their structure. Regardless of whether the three-dimensional pattern is inherent or generated by application of a forming process, the pattern is readily visible to the naked eye when the perpendicular distance between the viewer's eye and the plane of the web is about 12 inches. By way of contrast, the term "planar", when utilized herein to describe nonwovens and polymeric films, refers to the overall condition of the web when viewed by the naked eye on a macroscopic scale. In this context "planar" webs may include webs having fine-scale surface aberrations on one or both sides, the surface aberrations not being readily visible to the naked eye when the perpendicular distance between the viewer's eye and the plane of the web is about 12 inches or greater.

35 One macroscopically expanded, three-dimensional apertured polymeric web which is particularly well suited to transferring liquid deposited on one surface thereof to its opposite surface and thereafter isolating the transferred liquid from a wearer's skin is disclosed in commonly assigned U.S. Patent No. 3,929,135 issued to Thompson on Dec. 30, 1975, the disclosure of which is incorporated by reference

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herein. Thompson describes a macroscopically expanded, three dimensional web (e.g., a topsheet) comprised of liquid impermeable material, but provided with a pattern of tapered capillaries, the capillaries having a base opening in the plane of the topsheet and an apex opening remote from the plane of the topsheet, the apex opening being in intimate contact with the absorbent pad utilized in the disposable absorbent article. The Thompson topsheet allows the free transfer of liquids from the wearer's body into the absorbent element of the device while inhibiting the reverse flow of these liquids. This provides a relatively much drier surface in contact with the user than had previously been obtainable. Another macroscopically expanded, three-dimensional apertured plastic web well suited for use as a topsheet on absorbent articles such as sanitary napkins is disclosed in commonly assigned U.S. Patent No. 4,342,314 issued to Radel et al. on Aug. 3, 1982, the patent being hereby incorporated by reference herein. The macroscopically expanded, three-dimensional plastic web disclosed in the Radel patent exhibits a fiber-like appearance and tactile impression which has been favorably received by consumers when used as a wearer contacting surface. According to the teachings of the commonly assigned patents to Thompson and to Radel, et al., plastic webs of the aforementioned type can be made by applying a pressure differential to the web while it is supported on a three-dimensional forming structure until the web is macroscopically expanded to comply with the three-dimensional cross-section of the forming structure on which it is supported. When aperturing of the macroscopically expanded, three-dimensional web is desired, the pressure (vacuum is described) differential is applied continuously until such time as aperturing of the web in areas coinciding with the apertures in the forming structure has been completed.

A multi-phase, liquid-based process such as that described in U.S. Patent No. 4,609,518, issued September 2, 1986 to Curro et al. (hereafter referred to as "'518 patent'"), was also developed to provide a film with very small and very large apertures immediately adjacent one another. As the patent discloses, the formation of the very small (including micro-sized) apertures in the direction opposite those formed for large apertures hinders the ability of initially unabsorbed liquid from running off the web's surface. Thus, liquid not immediately transported through the large apertures is restrained from running off the web's surface, and is subsequently taken up through the larger apertures and is deposited in the article's core where the web is used as a topsheet material. These outwardly formed small apertures also reduce the level of web/skin contact and reduce the rigidity of the film, and thereby feel more comfortable to the user. Wearers have reported that such topsheets have a soft silky surface. Alternatively, the '518 patent discloses films where the very small apertures are formed in the same direction as the macro-apertures.

Regardless of the means employed for aperture formation, where a wettable film material is desired, the above references generally obtain such a structure by surface treating the naturally hydrophobic polymeric web with a wetting agent. Surface treatment is generally accomplished by either spraying surfactant onto the web's surface or by dipping the web in a surfactant-containing bath. Regardless of which of these methods is employed, surface treatment suffers from the inability to precisely control the location and level of treatment, as well as adverse effects caused by migration of significant amounts of surfactant into apertures and other components (e.g., absorbent core) when the apertured film is used as a topsheet in an absorbent article. Surface treatment further suffers from the disadvantage that desirable

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75 wetting agents, or surfactants, tend to be washed off upon repeated exposure to such liquids. Thus, when used as a topsheet in an absorbent article, the treated films lose their ability to transport liquid away from the skin and into the article's core after repeated wettings.

U.S. Patent No. 4,535,020, issued to Thomas et al. on August 13, 1985, addresses some of the problems associated with surface treating vacuum-formed apertured films by incorporating hydrophilic surfactant in the polymeric resin before extrusion for film formation (referred to herein as "resin incorporated surfactant", or "RIS"). (See also commonly assigned U.S. Patent Application Serial No. 80 08/713,377, filed September 13, 1996 by Y. P. Lee, et al.; U.S. Patent No. 4,923,914 to Nohr et al., issued May 8, 1990; U.S. Patent No. 5,057,262 to Nohr et al., issued October 15, 1991; U.S. Patent No. 5,120,888 to Nohr et al., issued June 9, 1992.) According to the teachings of Thomas, after extrusion of the resin/surfactant mixture, and subsequent formation of the apertures, the incompatible surfactant eventually 85 blooms to the film's surface to provide a more durably wettable web. However, as with surface treatment, RIS suffers from some degree of surfactant wash-off during use and/or during manufacture, particularly if liquid pressure differentials are used to form the web's apertures. Also, hydrophilic webs formed using RIS techniques are not immediately wettable, and depending on the relationship between the resin and the surfactant and environmental conditions, may not become wettable for finite periods of time. Similarly, 90 when such webs are used in absorbent articles, there will be some time delay before surfactant (that is washed off during wear) is replenished at the web's surface.

In spite of the teachings of the prior art, there remains a need for a liquid pervious web or film material that offers improved durable wettability after the passage of time and/or after exposure to liquid insults. Such materials have particular suitability for use in disposable absorbent structures. There also 95 remains the need for a process that provides such a durably wettable, liquid pervious web.

Accordingly, it is an object of the present invention to provide a liquid pervious web having improved durable wettability. This durable wettability is attained by applying a plasma-induced hydrophilic coating onto at least one surface of the starting web, to render the resulting web durably hydrophilic.

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SUMMARY OF THE INVENTION

The present invention relates to a durably wettable, liquid pervious web that is particularly useful as a topsheet material for absorbent articles. In one respect, the inventions relates to a durably-wettable, liquid pervious web which comprises:

- 105 (i) a web selected from the group consisting of polymeric films and nonwovens;
- (ii) a substantially continuous hydrophilic coating, less than about 2.5 microns thick, on at least one surface of the web, wherein said hydrophilic coating is applied to the web by plasma polymerization;

wherein at least one surface of the durably-wettable, liquid pervious web has a Post Aging contact angle

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110 that is not more than about 60 degrees greater than the Pre Aging contact angle.

In a similar aspect respect, at least one surface of the treated web will have a Post Washing contact angle that is not more than about 60 degrees greater than the Pre Washing contact angle. Preferably, both conditions will exist in a single web.

The invention also relates to an absorbent article comprising a durably wettable, liquid pervious
115 topsheet, the topsheet comprising a web and a hydrophilic coating on at least one surface of the web, wherein the hydrophilic coating is applied to the substrate by plasma polymerization.

Finally, the invention relates to a plasma polymerization process for making the durably wettable, liquid pervious webs described herein.

DETAILED DESCRIPTION OF THE INVENTION

120 I. Durably Wettable, Liquid Pervious Webs

As discussed in detail below, the present invention relates to a durably wettable web that is prepared by applying a hydrophilic coating to a starting polymeric film or nonwoven, using a plasma polymerization process.

As used herein, the term "web" refers to the starting substrate (i.e., a polymeric film or nonwoven)
125 to which the hydrophilic coating is applied. In contrast, the terms "durably wettable, liquid pervious web" or "treated web" refer to the final product - the polymer film or nonwoven having the durable hydrophilic coating.

As used herein, the term "liquid pervious" refers to the ability of a web or treated web to transport liquids from one surface of the web or treated web to the opposite surface of the web or treated web in a
130 sufficiently efficient manner so as to allow the treated web to be used as a component of a disposable article. Webs may be inherently liquid pervious or may be made liquid pervious by application of a processing step, such as, aperturing.

As used herein, the term "substantially continuous" means sufficiently continuous to provide the hydrophilic or wettable properties as defined by the stated or claimed contact angle limitations.

As used herein, the terms "hydrophilic" and "wettable" are used interchangeably and refer to
135 surfaces that are wettable by aqueous liquids (e.g., aqueous body liquids) deposited on these surfaces. Hydrophilicity and wettability are typically defined in terms of contact angle and the surface tension of the liquids and solids involved. This is discussed in detail in the American Chemical Society publication entitled Contact Angle, Wettability and Adhesion, edited by Robert F. Gould (Copyright 1964). A web
140 surface is said to be wetted by a liquid (i.e., hydrophilic) when either the contact angle between the liquid and the web surface is less than 90°, or when the liquid tends to spread spontaneously across the surface of the web, both conditions normally co-existing. Conversely, a surface is considered to be hydrophobic if the contact angle is greater than 90° and the liquid does not spread spontaneously across the surface of the web. In general, the lower the contact angle between the surface and the liquid, the more hydrophilic the surface.

145 The durably wettable, liquid pervious webs of the present invention are "durably wettable", insofar as the hydrophilic character engendered to the otherwise more hydrophobic film is maintained over time

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and after exposure to liquids. As discussed above, prior approaches directed at making hydrophobic films wettable result in initial improvements in wettability, but suffer from the negative attribute that wettability is lost over time and/or exposure to liquids. While not being bound by theory, it is believed that typical hydrophilic polymer and surface-treated polymer systems, such as corona discharge treatments, go through a "hydrophobic recovery" process. During the hydrophobic recovery process, surface wettability tends to decay over time because thermodynamics favors the exposure of lower surface energy molecular chain segments at polymer surface. Upon aging, hydrophilic molecular segments reorient and embed themselves and expose hydrophobic segments at polymer surface. If chemical crosslinking is induced at the polymer surface, the crosslinking tends to limit polymer chain mobility, thus significantly slowing the "hydrophobic recovery" process and therefore preserving polymer surface wettability over time. Since Applicants' invention provides for polymer chemical crosslinking, via a radiation curing process, a durably wettable, liquid pervious web can be produced.

Durable wettability is described herein in terms of the ability of a durably wettable, liquid pervious web (as indicated, also referred to herein as a "treated web", to distinguish from the starting more hydrophobic "web") to retain its wettable character after aging (referred to as "Post Aging") and/or after exposure to liquids (referred to as "Post Washing"). The methods for measuring Post Aging contact angle and Post Washing contact angle are discussed below.

As indicated, the durable wettability of the present durably wettable, liquid pervious webs is attained by use of a plasma process. Plasma is often referred to as the fourth state of matter. When energy is applied to a solid (e.g., a polymeric film or nonwoven), the solid can undergo a transition to the liquid state. If further energy is applied, the liquid becomes a gas. If additional energy of the proper kind is applied, the gas dissociates and becomes plasma. Plasmas exist in a variety of forms. The preferred plasma useful herein is a low pressure or vacuum process, which allows processing of the web at or near ambient temperature, i.e., about 20°C. This prevents thermal degradation of the web being processed and/or thermal distortion of the formed web that is being treated. Within the plasma chamber where the web is to be treated, active species in the form of electrons, free-radicals, ions and energetic neutrals collide with the surface of the web, e.g. polymer, breaking molecular bonds and creating new functional groups on the surface. These active and energetic species also react in the gas phase, resulting in a thin coating being deposited on at least one surface of the web.

Suitable plasma systems for use in the present invention incorporate a parallel plate electrode design where materials to be treated are exposed directly to the primary field of RF energy, but are not part of the circuitry. The subsequent primary plasma is particularly more uniform and more efficient since the part is exposed in all three dimensions to the glow discharge. With higher pressure processes (but still within the general definition of a cold gas plasma), some form of gas delivery system, designed to create a uniform laminar flow of process gas throughout the entire chamber volume is beneficial. In multiple electrode/shelf designs, it is important that each of the electrodes receive equal amounts of RF energy. In this manner a uniform glow discharge is created between each shelf or in each plasma zone. Solid state components and microprocessor control of the system parameters of process time, flow rate, power level,

185 and working pressure, will also ensure process uniformity, efficiency, and repeatability.

Since plasmas are electrically conductive atmospheres, they carry a characteristic impedance to the output of the RF generator. Therefore, the preferred plasma process utilizes a matching network to constantly tune the plasma impedance to the output impedance of the RF generator. Advanced plasma systems suitable for use in the present invention are available from HIMONT Plasma Science, Foster City, Calif. (a business unit of HIMONT U.S.A., Inc.), and incorporate an automatic matching type of network and provisions for error checking during the process.

The low temperature plasma is generated in a gaseous atmosphere at reduced pressure of from about 0.001 to about 10 Torr, preferably from about 0.01 to about 5 Torr, more preferably from about 0.05 to about 1 Torr, and most preferably from about 0.05 to about 0.4 Torr. The electric power can be supplied to the equipment at a high radio frequency, from about 40 KHz to about 3 GHz, preferably from about 13 to about 27 MHz, and most conveniently at about 14 MHz. To achieve the desired plasma condition in the gaseous atmosphere, the electric power delivered to the apparatus can vary over a range of from about 10 to about 10,600 watts; preferably from about 50 to about 5,000 watts, more preferably from about 250 to about 3000 watts, most preferably from about 500 to about 2500 watts. The power used is somewhat dependent on the chamber's working volume. The most preferred range of about 500 to about 2500 watts is appropriate for HIMONT Plasma Science PS0500D gas plasma apparatus with a working volume of about 5.0 cubic feet. The plasma treatment time varies from a few seconds to several minutes, preferably from about 20 seconds to about 30 minutes, most preferably from about 60 seconds to about 20 minutes.

It should be appreciated that treatment pressure, time and power are interrelated, rather than independent, variables. The effect of the level selected for each of these variables will determine the extent of web surface modification and/or coating thickness; also related are the chamber volume and geometry as well as the sample size and surface geometry. The selection of the level for these variables is well within the ordinary skill of practitioners in the art to which this invention pertains.

The hydrophilic coating layer is deposited onto the surface of a suitable web (either previously apertured or unapertured) by low temperature plasma-induced vapor deposition (i.e., polymerization) of a monomer or a combination of monomers, such that a hydrophilic coating will be applied to the web. In a preferred embodiment, the monomers will be silicon-containing compounds having one to three silicon atoms, which compounds are selected from the group consisting of (i) silanes of the formula SiR_4 , where each R is the same or different and is selected from H; a C_1 - C_8 linear or branched alkyl or alkoxy; a C_6 - C_{10} aryl, unsubstituted or substituted with C_1 - C_4 linear or branched alkyl; a vinyl radical, i.e. $-\text{CH}=\text{CH}_2$; or a C_3 - C_8 allyl radical; provided that when R is H only one or two Rs are H; (ii) organosilicones based on a structure consisting of alternate silicon and oxygen atoms with various organic radicals attached to the silicon having the formula $\text{R}'\text{R}''\text{R}'''\text{Si}[-\text{O}-\text{Si}(\text{R}')(\text{R}'')]_n-\text{R}'''$, where R' , R'' and R''' can be the same or different and are C_1 - C_8 linear or branched alkyl or alkoxy, R' and R'' can also be hydrogen provided that no more than 50% of the R' and R'' groups are hydrogen, and n is 1, 2 or 3; and (iii) mixtures thereof.

Representative silicon compounds include, but are not limited to, hexamethyldisiloxane (HMDSO), methyltrimethoxy silane (MTMS), vinyltrimethoxy silane (VTMS), vinyltriethoxy silane

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(VTES), ethylmethoxy silane (EMS), ethyltrimethoxy silane (ETMS), tetraethoxy silane (TES), cyclohexylmethyl-dimethoxy silane (CMDMS), dicyclopentyl-dimethoxy silane (DCDMS), phenyltriethoxy silane (PES), diphenyldimethoxy silane (DPDMS), tetramethyldisiloxane (TMDSO), and hexamethyltrisiloxane (HMTSO). The silicon compounds employed are introduced into the plasma deposition chamber in the gaseous state. Prior to being introduced into the chamber, the silicon compound is heated to a temperature of from about 40° to about 100°C, generally from about 40° to about 60°C, to vaporize the compound and create sufficient vapor pressure such that the coating is deposited at a reasonable speed. Oxygen in gaseous form and argon are fed into the deposition chamber simultaneously with, but each with a separate feeding means and mass flow controller, the gaseous silicon compound. Depending upon the application, the O₂ flow rate ranges from about 25 standard cubic centimeter/minute ("sccm") to about 1200 sccm, the gaseous silicon compound flow is from about 10 sccm to about 250 sccm, and Ar flow is from about 1 sccm to about 150 sccm. Argon is used to enhance the rate of deposition of the gaseous materials being employed and, therefore, it is preferable to use Argon in the process. With respect to the flow rates for argon and oxygen versus the monomer (e.g. HMDSO) flow rate, the following are preferred: assuming that the mass flow Q1 represents 3% argon and 97 % oxygen and vapor mass flow Q2 represents the mass flow for the monomer, the preferred ratio of Q1:Q2 is from about 10:1 to about 1:2, more preferred is from about 5:1 to about 1:1, and most preferred is about 3:2.

Oxygen is essential to the plasma deposition process with the silicon compounds according to this invention. Without oxygen, it is not possible to obtain a plasma-induced hydrophilic coating using the aforementioned silicon compounds. Whatever oxidizing effect it has, it appears to be necessary to utilize oxygen if one is to obtain the hydrophilic coatings of this invention.

The total vapor pressure of the gaseous materials introduced into the plasma deposition chamber for the deposition of the hydrophilic coating layer is about 0.04 to about 0.5 Torr, preferably about 0.35 to about 0.45 Torr, most preferably about 0.4 Torr. The process pressure must be such that a low bias potential on the RF-driven electrode is achieved. The total vapor pressure for the hydrophilic coating layer is from about 0.04 to about 0.4 Torr, preferably from about 0.06 to about 0.13 Torr, depending on the process used and the substrate being treated.

Alternatively, monomer deposition may be achieved via the flash vaporization technique that is described in U.S. Patent No. 4,842,893 issued to Yializis on Apr. 29, 1988, the disclosure of which is incorporated by reference herein.

The web to be subjected to plasma polymerization may be flat (two dimensional) or complex (three dimensional, including previously apertured films and nonwovens). That is, plasma treatment may be conducted either before or after formation of the apertures of the web. In a preferred embodiment, plasma treatment will be conducted after aperture formation, so as to better preserve a uniform hydrophilic coating on the web's surface.

The aforementioned advanced plasma systems available from HIMONT Plasma Science, such as the PS0500D reactor are equipped with a throttle valve, thereby making it possible to achieve a range of process pressures with the same gas flow rate.

The plasma treatment time for obtaining the desired hydrophilic coatings is from typically about 1 minute to about 10 minutes, preferably about 1.5 to about 4 minutes, most preferably about 1.5 to about 2.5 minutes; and the RF power used to cause reaction of the vapor is typically from about 200 to about 1500 watts, preferably about 1000 to about 1400 watts, most preferably about 1100 to about 1300 watts. The RF power typically employs ranges from about 1200 to about 2500 watts and depends on the substrate being treated and the throughput requirements. The resulting hydrophilic coatings can be produced in different thicknesses, but are typically from about 0.1 to about 2.5 microns, preferably about 1 to about 2 microns.

As indicated, the plasma induced hydrophilic coating exhibits a contact angle for water of less than about 90 degree, such that any water placed on the treated web will tend to spread spontaneously over the treated web's coated surface. In a preferred embodiment, the treated web may be further treated by exposure to a low temperature plasma gas composition (also referred to herein as a "surface modifying gas stream") or an energy source (also referred to herein as "radiation curing") such as an apparatus that emits, including but not limited to, infra red, electron beam, thermionic or ultra violet radiation. Apparatuses that are suitable as energy sources in the present invention are disclosed in U.S. Patent No. 4,842,893 issued to Yializis on Apr. 29, 1988, the disclosure of which is incorporated by reference herein.

In the surface modifying gas stream embodiment the gas stream preferably comprises N_2O and CO_2 , to enhance the durability of the hydrophilic coating. In one such preferred embodiment, the plasma gas composition will comprise from about 80 to about 40 mol % N_2O and from about 20 to about 60 mol % CO_2 , preferably from about 70 to about 45 mol % N_2O and from about 30 to about 55 mol % CO_2 , most preferably from about 60 to about 45 mol % N_2O and from about 40 to about 55 mol % CO_2 , where the amount of N_2O and CO_2 in the mixture equals 100 to 10 mol %, for a time sufficient to modify the surface of the hydrophilic coating to enhance its durability.

In the radiation curing embodiment, the radiation source is preferably a gas discharge electron beam gun. The gun directs a flow of electrons through a emitter window onto the monomer, thereby further curing the monomer, which enhances the durability of the hydrophilic coating. Curing is controlled by matching the electron beam voltage to the dielectric thickness of the monomer coating. For example, a 10 Kv electron voltage will penetrate about 1 micron of deposited monomer.

The plasma process is generally practiced as follows. The starting web to be treated is placed into a vacuum chamber and the chamber pressure is reduced, typically to about 0.005 Torr. The process gas or gas mixture employed is introduced to the chamber and the chamber pressure is stabilized at a pressure of 0.04-0.4 Torr. The interior dimension of the work area is approximately 1.73 X 0.76 X 1.02 meters (width x height x depth) for a total working volume of 1.34 cubic meters. A suitable high frequency form of energy, typically 13.56 MHz radio frequency energy, is used to create the plasma: in the system described, this is achieved with a total power input capacity of up to 2500 watts. The RF energy dissociates the gas, creating a plasma characterized by a distinctive glow. Since the process is conducted at reduced pressures, the bulk temperature of the gas is near ambient temperature, thus the reference to a cold gas plasma, a glow discharge, or a cold gas glow discharge. Because the web being subjected to the plasma conditions is located within the electric field, the process is referred to as direct plasma polymerization. In contrast, see

co-pending U.S. Patent Application Serial No. 09/157840, filed September 21, 1998 by P. France et al.,
300 titled DURABLY WETTABLE POLYMERIC WEBS PREPARED USING A REMOTE PLASMA
POLYMERIZATION PROCESS, which describes a process for making durably wettable webs using
"remote" plasma polymerization.) The electrons or ions created in the plasma bombard the web's surface,
abstracting atoms or breaking bonds, creating free radicals. These free radicals are unstable and seek to
satisfy a more stable state by reacting with free radicals or groups within the plasma gas, also establishing
305 new moieties on the surface of the web. In addition, the energetic electrons in the glow discharge fragment
the molecules in the gas phase, leading to complex chemical reactions that result in a thin hydrophilic
coating being deposited on at least one surface of the web.

Typically, and preferably, before plasma deposition of the hydrophilic coating onto the web, an
initial step is performed. The purpose of this step is to clean the web's surface to promote adhesion of the
310 subsequently deposited thin hydrophilic coating. Cleaning may be accomplished by subjecting the web's
surface to radiation (herein referred to as radiation cleaning) from an energy source including but not
limited to, infra red, electron beam, thermionic or ultra violet radiation or by plasma cleaning. Apparatuses
that are suitable as energy sources in the present invention are disclosed in U.S. Patent No. 4,842,893
issued to Yializis on Apr. 29, 1988. In the radiation cleaning embodiment, the radiation source is
315 preferably a gas discharge electron beam gun. The gun directs a flow of electrons through a emitter
window onto the web's surface, thereby abstracting atoms or breaking bonds, thus creating free radicals.
These free radicals are unstable and seek to satisfy a more stable state thus they serve as bonding sites for
the monomers that are used to produce the web's hydrophilic coating. Cleaning is controlled by matching
the electron beam voltage to the dielectric thickness or depth of cleaning that is desired. For example, a 10
320 Kv electron voltage will penetrate to a web depth of about 1 micron.

In the plasma cleaning embodiment, the gases are usually either Ar alone, O₂ alone, or mixtures
(e.g., 1:1 ratio) of Ar and O₂. Gas flow rates are typically in the range of about 20 to about 100 sccm
(standard cc/min), preferably about 40 to about 80 sccm, and most preferably about 50 to about 60 sccm.
RF power is approximately 1100 watts, and process pressure is about 0.040 Torr.

325 After the optional initial step, the next step is the plasma deposition of the hydrophilic coating, as
described above and in more detail in the examples below. Often, but not always, a step subsequent to the
CO₂ and N₂O surface treating step is used to enhance the durability or uniformity of the plasma coating.
Useful process gases are Ar and/or O₂. Process times are usually about 1 to about 3 minutes, with about 2
minutes typically being optimum. Gas flows range from about 40 to about 250 sccm, with process
330 pressures from about 0.200 to about 0.400 Torr, and RF input power from about 150 to about 1500 watts.

The materials useful as polymeric films to be plasma treated to provide a hydrophilic coating will
be derived from thermoplastic polymers. In general, the term "thermoplastic polymer" is used herein to
mean any thermoplastic polymer which can be used for the preparation of films. Examples of
thermoplastic polymers include, by way of illustration only, end-capped polyacetals, such as
335 poly(oxymethylene) or polyformaldehyde, poly(trichloroacetaldehyde), poly(n-valeraldehyde),
poly(acetaldehyde), poly(propionaldehyde), and the like; acrylic polymers, such as polyacrylamide,

poly(acrylic acid), poly(methacrylic acid), poly(ethyl acrylate), poly(methyl methacrylate), and the like; fluorocarbon polymers, such as poly(tetrafluoroethylene), perfluorinated ethylene-propylene copolymers, ethylene-tetrafluoroethylene copolymers, poly(chlorotrifluoroethylene), ethylene-chlorotrifluoroethylene copolymers, poly(vinylidene fluoride), poly(vinyl fluoride), and the like; polyamides, such as poly(6-aminocaproic acid) or poly(ϵ -caprolactam), poly(hexamethylene adipamide), poly(hexamethylene sebacamide), poly(11-aminoundecanoic acid), and the like; polyaramides, such as poly(imino-1,3-phenyleneiminoisophthaloyl) or poly(m-phenylene isophthalamide), and the like; polyarylenes, such as poly-p-xylylene, poly(chloro-p-xylylene), and the like; polyaryl ethers, such as poly(oxy-2,6-dimethyl-1,4-phenylene) or poly(p-phenylene oxide), and the like; polyaryl sulfones, such as poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene-isopropylidene-1,4-phenylene), poly(sulfonyl-1,4-phenyleneoxy-1,4-phenylene-sulfonyl-4,4'-biphenylene), and the like; polycarbonates, such as poly(bisphenol A) or poly(carbonyldioxy-1,4-phenylene-isopropylidene-1,4-phenylene), and the like; polyesters, such as poly(ethylene terephthalate), poly(tetramethylene terephthalate), poly(cyclohexylene-1,4-dimethylene terephthalate) or poly(oxymethylene-1,4-cyclohexyl-enemethyleneoxyterephthaloyl), and the like; polyaryl sulfides, such as poly(p-phenylene sulfide) or poly(thio-1,4-phenylene), and the like; polyimides, such as poly(pyromellitimido-1,4-phenylene), and the like; polyolefins, such as polyethylene, polypropylene, poly(1-butene), poly(2-butene), poly(1-pentene), poly(2-pentene), poly(3-methyl-1-pentene), poly(4-methyl-1-pentene), 1,2-poly-1,3-butadiene, 1,4-poly-1,3-butadiene, polyisoprene, polychloroprene, polyacrylonitrile, poly(vinyl acetate), poly(vinylidene chloride), polystyrene, and the like; copolymers of the foregoing, such as acrylonitrile-butadiene-styrene (ABS) copolymers, and the like.

Preferred polymers are polyolefins and polyesters, with polyolefins being more preferred. Even more preferred are those polyolefins which contain only hydrogen and carbon atoms and which are prepared by the addition polymerization of one or more unsaturated monomers. Examples of such polyolefins include, among others, polyethylene, polypropylene, poly(1-butene), poly(2-butene), poly(1-pentene), poly(2-pentene), poly(3-methyl-1-pentene), poly(4-methyl-1-pentene), 1,2-poly-1,3-butadiene, 1,4-poly-1,3-butadiene, polyisoprene, and the like. In addition, such term is meant to include blends of two or more polyolefins and random and block copolymers prepared from two or more different unsaturated monomers. Because of their commercial importance, the most preferred polyolefins are polyethylene and polypropylene.

In addition to polymeric films, webs that can be used to produce the durably wettable, liquid pervious webs of the present invention include but are not limited to spun bonded, hydroentangled, needled and polymericly bound nonwovens. Suitable nonwoven webs are typically formed from organic textile fibers including but not limited to cotton, wool, wood, jute, viscous rayon, nylon, polyester, polyolefins, carbon, or mixtures thereof. Inorganic fibers such as glass and metal can be used alone or in combination or further combined with organic fibers. In the case of staple fibers, fiber length varies from about 1/4 inch to about 2 or more inches. In the case of spun bonded webs, the fiber lengths are indefinite. The staple fibers used in hydroentangled, needled and polymericly bound nonwovens are processed through conventional textile machinery.

375 For example, in producing a polymericly bound, nonwoven web, a carding machine may be used
to form a continuous length of rather two-dimensional loosely associated fibers known as a carded web.
These webs may be assembled to form a multiple layer or three-dimensional fibrous web of significant
weight, e.g., from about several grams to thousands of grams per yard. In continuous nonwoven fibrous
webs, the textile fibers are arrayed at various angles to the lengthwise axis of the web. When a web is
380 formed by the action of a carding machine, the fibers are usually predominantly oriented in the machine
direction and, on the other hand, isotropic webs may be formed such as by air-laying. The fibrous webs
described above are typically impregnated with a polymeric binding agent (polymericly bound). In a
preferred form, the polymeric binders are applied as emulsions of acrylic, polyvinylacetate, or similar
polymeric nature, and mixtures thereof. Preferably, the fibers are unwoven and substantially haphazardly
385 oriented and adhesively bonded together with polymeric binder.

Hydroentangled and needled webs are distinct from polymericly bound webs as they rely
principally on the physical entanglement of their fibers to provide web integrity. In contrast to polymericly
bound and physically entangled webs, spun bond webs typically are composed of fibers of infinite length
that are bound together through solvent or melt processes.

390 As indicated, the webs may be in the form of a flat film or may be a previously apertured three
dimensional film. The coatings are durable and increase the surface energy of the web to render the treated
web more wettable. The coating is durable, in that it is maintained over time, even after exposure to water
or other aqueous liquids. In this regard, the webs of the present invention are described in one respect in
terms of their ability to remain wettable over time and/or after exposure to liquids. The ability to remain
395 wettable over time is assessed by measuring the web's Post Aging contact angle. This measurement
involves storing the treated web at 60° C for 16 hours, to artificially age the treated web, before measuring
contact angle. The ability to remain wettable after exposure to liquids is assessed by measuring the web's
Post Washing contact angle. This measurement involves placing a 2 in. x 2 in. sample of treated web in a
250 ml water bath at 65° C for 90 sec. with vigorous agitation prior to measuring contact angle. Procedures
400 and devices for measuring contact angle between a liquid and a web surface are well known in the art.
However, water contact angle, measured with a goniometer (Model # 100-00, Rame-Hart, Inc., Mountain
Lakes, NJ), is used to assess the web wettability of the present invention. All contact angle measurements
are reported as the average measurements on 3 samples.

In one aspect, the treated web of the present invention will have a Post Aging contact angle that is
405 not more than about 60 degrees greater than the treated web's Pre Aging contact angle (i.e., the contact
angle as measured before storage at 60° C for 16 hours). Preferably, the treated web will have a Post Aging
contact angle that is not more than about 40 degrees, more preferably not more than about 20 degrees, still
more preferably not more than about 10 degrees, greater than the Pre Aging contact angle. In another
respect, the treated web of the present invention will have a Post Washing contact angle that is not more
410 than about 60 degrees greater than the treated web's Pre Washing contact angle (i.e., the contact angle as
measured before the treated web is placed in a 250 ml water bath at 65° C for 90 sec with vigorous
agitation). In this regard, the treated web will preferably have a Post Washing contact angle that is not

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more than about 40 degrees, more preferably not more than about 20 degrees, still more preferably not more than about 10 degrees, greater than the Pre Washing contact angle. In a preferred aspect, the treated web of the present invention will exhibit both the Post Aging and Post Washing requirements discussed above.

The treated webs of the present invention will exhibit either (preferably both) a Post Aging or a Post Washing contact angle of less than about 90 degrees, preferably not more than about 70 degrees, more preferably not more than about 50 degrees, still more preferably not more than about 30 degrees, and most preferably not more than about 20 degrees.

II Absorbent Articles

As used herein, the term "absorbent article" refers generally to devices used to absorb and contain body exudates, and more specifically refers to devices which are placed against or in proximity to the body of the wearer to absorb and contain the various exudates discharged from the body. The term "absorbent article" is intended to include diapers, catamenial pads, tampons, sanitary napkins, incontinent pads, training pants and the like, as well as wipes, bandages and wound dressings. The term "disposable" is used herein to describe absorbent articles which are not intended to be laundered or otherwise restored or reused as an absorbent article (i.e., they are intended to be discarded after limited use, and, preferably, to be recycled, composted or otherwise disposed of in an environmentally compatible manner). A "unitary" absorbent article refers to absorbent articles which are formed as a single structure or as separate parts united together to form a coordinated entity so that they do not require separate manipulative parts such as a separate holder and pad.

It is to be understood that the overall size, shape, and/or configuration of the absorbent article, if any, into which the treated webs according to the present invention are incorporated, or utilized in conjunction with, have no criticality or functional relationship to the principles of the present invention. Such parameters, however, must be considered along with the intended liquid and intended functionality when determining appropriate web configurations.

In addition to the treated webs of the present invention, absorbent articles will also comprise an absorbent core for retention of any absorbed body liquids. Exemplary absorbent structures for use as the absorbent core in the present invention are described in U.S. Patent No. 4,950,264 issued to Osborn on August 21, 1990; U.S. Patent No. 4,610,678 issued to Weisman et al. on September 9, 1986; U.S. Patent No. 4,834,735 issued to Alemany et al. on May 30, 1989; European Patent Application No. 0 198 683, the Procter & Gamble Company, published October 22, 1986 in the name of Duenk et al.; U.S. Patent No. 4,673,402 issued to Weisman et al. on June 16, 1987; and U.S. Patent No. 4,888,231 issued to Angstadt on December 19, 1989. The absorbent core may further comprise the dual core system containing an acquisition/distribution core of chemically stiffened fibers positioned over an absorbent storage core as detailed in U.S. Patent No. 5,234,423, entitled "Absorbent Article With Elastic Waist Feature and Enhanced Absorbency" issued to Alemany et al., on August 10, 1993; and in U.S. Patent No. 5,147,345, entitled

"High Efficiency Absorbent Articles For Incontinence Management" issued to Young, LaVon and Taylor on September 15, 1992. The disclosure of all of these patents is incorporated herein by reference.

A preferred embodiment of a unitary disposable absorbent article made in accordance herewith is a catamenial pad, or sanitary napkin. As used herein, the term "sanitary napkin" refers to an absorbent article which is worn by females adjacent to the pudendal region, generally external to the urogenital region, and which is intended to absorb and contain menstrual liquids and other vaginal discharges from the wearer's body (e.g., blood, menses, and urine). Interlabial devices which reside partially within and partially external to the wearer's vestibule are also within the scope of this invention. Suitable feminine hygiene articles are disclosed in U.S. Patent No. 4,556,146, issued to Swanson et al. on Dec. 3, 1985, U.S. Patent No. 4,589,876, issued to Van Tilberg on April 27, 1993, U.S. Patent No. 4,687,478, issued to Van Tilburg on Aug. 18, 1987, U.S. Patent No. 4,950,264, issued to Osborn, III on Aug. 21, 1990, U.S. Patent No. 5,009,653, issued to Osborn, III on April 23, 1991, U.S. Patent 5,267,992, issued to Van Tilburg on Dec. 7, 1993, U.S. Patent No. 5,389,094, issued to Lavash et al. on Feb. 14, 1995, U.S. Patent No. 5,413,568, issued to Roach et al. on May 9, 1995, U.S. Patent No. 5,460,623, issued to Emenaker et al. on Oct. 24, 1995, U.S. Patent No. 5,489,283, issued Van Tilburg on Feb. 6, 1996, U.S. Patent No. 5,569,231, issued to Emenaker et al. on Oct. 29, 1996, and U.S. Patent No. 5,620,430, issued to Bamber on April 15, 1997, the disclosure of each of which is incorporated by reference herein.

In a preferred embodiment of the present invention, the sanitary napkin has two flaps each of which are adjacent to and extend laterally from the side edge of the absorbent core. The flaps are configured to drape over the edges of the wearer's panties in the crotch region so that the flaps are disposed between the edges of the wearer's panties and the thighs. The flaps serve at least two purposes. First, the flaps help serve to prevent soiling of the wearer's body and panties by menstrual liquid, preferably by forming a double wall barrier along the edges of the panty. Second, the flaps are preferably provided with attachment means on their garment surface so that the flaps can be folded back under the panty and attached to the garment facing side of the panty. In this way, the flaps serve to keep the sanitary napkin properly positioned in the panty. The flaps can be constructed of various materials including materials similar to the topsheet, backsheet, tissue, or combination of these materials. Further, the flaps may be a separate element attached to the main body of the napkin or can comprise extensions of the topsheet and backsheet (i.e., unitary). A number of sanitary napkins having flaps suitable or adaptable for use with the sanitary napkins of the present invention are disclosed in U.S. Patent No. 4,687,478 entitled "Shaped Sanitary Napkin With Flaps", which issued to Van Tilburg on August 18, 1987; and U.S. Patent No. 4,589,876 entitled "Sanitary Napkin", which issued to Van Tilburg on May 20, 1986. The disclosure of each of these patents is hereby incorporated herein by reference.

In a preferred embodiment of the present invention, an acquisition layer(s) may be positioned between the topsheet and the absorbent core. The acquisition layer may serve several functions including improving wicking of exudates over and into the absorbent core. There are several reasons why the improved wicking of exudates is important, including providing a more even distribution of the exudates throughout the absorbent core and allowing the sanitary napkin to be made relatively thin. The wicking

referred to herein may encompass the transportation of liquids in one, two or all directions (i.e., in the x-y plane and/or in the z-direction). The acquisition layer may be comprised of several different materials including nonwoven or woven webs of synthetic fibers including polyester, polypropylene, or polyethylene; natural fibers including cotton or cellulose; blends of such fibers; or any equivalent materials or combinations of materials. Examples of sanitary napkins having an acquisition layer and a topsheet are more fully described in U.S. Patent No. 4,950,264 issued to Osborn and U.S. Patent Application Serial No. 07/810,774, "Absorbent Article Having Fused Layers", filed December 17, 1991 in the names of Cree, et al. The disclosures of each of these references are hereby incorporated herein by reference. In a preferred embodiment, the acquisition layer may be joined with the topsheet by any of the conventional means for joining webs together, most preferably by fusion bonds as is more fully described in the referenced Cree application.

Catamenial pads may be constructed as follows. Onto silicone-coated release paper a spiral pattern of H2031 Findlay hot melt adhesive is applied at 0.04 g/in^2 . This adhesive layer is transferred onto the top (wearer-facing) side of a secondary topsheet by rolling the secondary topsheet and coated release paper together with a hand roller. The secondary topsheet is formed of a nonwoven material known as Fort James Airlaid Tissue, Grade 817, commercially available from the Fort James Corp. of Green Bay, Wisconsin. A topsheet of the present invention is applied to the adhesive side of the secondary topsheet and the two are bonded by gently pressing them together with a hand roller. Two strips of one-quarter-inch double-sided tape are applied along both long edges of a polyethylene backsheet. The absorbent core is added to construct the complete absorbent structure.

As used herein, the term "diaper" refers to a garment generally worn by infants and incontinent persons that is worn about the lower torso of the wearer. It should be understood, however, that the present invention is also applicable to other absorbent articles such as incontinent briefs, incontinent pads, training pants, diaper inserts, facial tissues, paper towels, and the like. In general, a diaper of the present invention will comprise a liquid pervious topsheet of the present invention; a liquid impervious backsheet joined with the topsheet; and an absorbent core positioned between the topsheet and the backsheet. Additional structural features such as elastic members and fastening means for securing the diaper in place upon a wearer (such as tape tab fasteners) may also be included.

While the topsheet, the backsheet, and the absorbent core can be assembled in a variety of well known configurations, a preferred diaper configuration is described generally in U.S. Patent No. 3,860,003 (Buell), issued January 14, 1975, the disclosure of which is incorporated by reference. Alternatively, preferred configurations for disposable diapers herein are also disclosed in U.S. Patent No. 4,808,178 (Aziz et al.), issued February 28, 1989; U.S. Patent No. 4,695,278 (Lawson), issued September 22, 1987; and U.S. Patent No. 4,816,025 (Foreman), issued March 28, 1989, the disclosures of each of these patents hereby being incorporated herein by reference. Suitable incontinence articles for adult wearers are disclosed in U.S. Patent No. 4,253,461 issued to Strickland, et al. on March 3, 1981; U.S. Patent Nos. 4,597,760 and 4,597,761 issued to Buell; U.S. Patent No. 4,704,115; U.S. Patent No. 4,909,802 issued to Ahr, et al.; U.S. Patent No. 4,964,860 issued to Gipson, et al. on October 23, 1990; and in U.S. Patent

Application Serial No. 07/637,090 filed by Noel, et al. on January 3, 1991 (PCT Publication No. WO 92/11830 published on July 23, 1992). The disclosure of each of these references is incorporated herein.

530 The absorbent core of the diaper is positioned between the topsheet and the backsheet. The absorbent core can be manufactured in a wide variety of sizes and shapes (e.g., rectangular, hourglass, asymmetrical, etc.). The total absorbent capacity of the absorbent core should, however, be compatible with the design liquid loading for the intended use of the absorbent article or diaper. Further, the size and absorbent capacity of the absorbent core can vary to accommodate wearers ranging from infants through adults.

535 As indicated, the absorbent core may include a liquid distribution member. In a preferred configuration, the absorbent core preferably further includes an acquisition layer or member in liquid communication with the liquid distribution member and located between the liquid distribution member and the topsheet. The acquisition layer or member may be comprised of several different materials including nonwoven or woven webs of synthetic fibers including polyester, polypropylene, or polyethylene, natural
540 fibers including cotton or cellulose, blends of such fibers, or any equivalent materials or combinations of materials.

In a preferred embodiment, the diaper will comprise elasticized leg cuffs. The elasticized leg cuffs can be constructed in a number of different configurations, including those described in U.S. Patent No. 3,860,003; U.S. Patent No. 4,909,803, issued to Aziz et al. on Mar. 20, 1990; U.S. Patent No. 4,695,278,
545 issued to Lawson on Sep. 22, 1987; and U.S. Patent No. 4,795,454, issued to Dragoo on Jan. 3, 1989, each being incorporated herein by reference.

In use, the diaper is applied to a wearer by positioning the back waistband region under the wearer's back, and drawing the remainder of the diaper between the wearer's legs so that the front waistband region is positioned across the front of the wearer. The tape-tab or other fasteners are then secured
550 preferably to outwardly facing areas of the diaper.

III. Examples

The following examples are illustrative and are not meant as a limitation of the invention disclosed and claimed herein. With respect to Example 2, the mass flow controller used to deliver the silicon-containing monomer compound for the deposition processes was calibrated for the flow rate of HMDSO. The flow rates of other gases were calculated based on the specific heats of the respective gases. The accuracy of the mass flow controllers in these cases is $\pm 5\%$ or better.

Example 1

This example illustrates the plasma treatment process and benefit of this invention in applying a permanent hydrophilic coating to a flat polyethylene film. Flat polyethylene (PE) film having a 1 mil average thickness is obtained from Tredegar Film Products, Inc. (Terre Haute, IN) with material composition designation code X-8318-1. Three-step plasma treatments are conducted in a plasma reactor (Advanced Plasma System, Model D, radio frequency (RF) : 40 KHz), with the gas input and process conditions indicated in Table 1.

Table 1

Step #	Gas Input *	Flow Rate (sccm)**	RF Power (Watt)	Treatment Time (min)
1	Ar/O ₂	2/73	500	2
2	Ar/O ₂ /HMDSO	2/73/50	500	10
3	Ar/O ₂	2/73	500	1

*: Ar: Argon; O₂: oxygen; HMDSO: hexamethyl disiloxane

** : sccm: standard cm³/minute

The resulting plasma treated web samples are then tested for surface wettability both before and after rapid aging conditions. Rapid aging condition refers to conditioning the web sample at 60° C for 16 hours prior to wettability measurement. Water contact angle, measured with a goniometer (Model # 100-00, Rame-Hart, Inc., Mountain Lakes, NJ), is used to assess web wettability. Strong wetting durability of HMDSO-derived plasma coating is established, as demonstrated by comparable contact angles seen between pre-aged and post-aged samples (see Table 2).

Table 2

Sample	Water Contact Angle* (degrees)	
	Pre-Aged	Post-Aged
Untreated PE film	96 (3)	96 (3)
HMDSO-plasma treated PE web	26 (1)	26 (3)

*: Contact angle measured 3 times on the same treated web is averaged and standard deviation is reported in parenthesis.

Example 2

This example illustrates the alternate plasma treatment process and benefit of this invention in applying a permanent hydrophilic coating to a flat PE film. Flat PE film having a 1 mil average thickness is obtained from Tredegar Film Products, Inc. (Terre Haute, IN) with material composition designation

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580 code X-8318-1. Three-step plasma treatments are conducted in a plasma reactor (Plasma Science PS0500D), with gas input and process conditions indicated in Table 3.

Table 3

Step #	Gas Input **	Flow Rate (sccm)*	RF Power (Watt)	Treatment Time (min)
1	Ar	58	1080	1
2	Ar/O ₂ /HMDSO	43/1560/52	1200	2
3	N ₂ O/CO ₂	200/207	1325	2

* sccm : standard cm³/minute

** Ar: Argon; O₂: oxygen; HMDSO: hexamethyl disiloxane; N₂O: nitrous oxide;

585 CO₂: carbon dioxide

The resulting plasma treated web samples are then evaluated for surface wettability before and after the water wash test. Water wash test refers to immersing a 2 in. x 2 in. web sample in a 250 ml water bath at 65° C for 90 sec with vigorous agitation (with a Teflon coated stir bar). Water contact angle, measured with a goniometer (model # 100-00, Rame-Hart, Inc., Mountain Lakes, N.J.), is used to assess the webs' wettability. Strong wetting durability of HMDSO-derived plasma coating is established, as is demonstrated by comparing contact angle between pre-washed and post-washed samples (see Table 4).

Table 4

Sample	Water Contact Angle * (degrees)	
	Pre-washed	Post-washed
Untreated PE Film	96 (3)	96 (3)
HMDSO-plasma treated PE Web	7 (1)	14 (1)

*: contact angle measured 3 times on the same film/web is averaged and standard deviation is reported in parenthesis.

595 While specific embodiments of the invention have been described in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as described and claimed.

What is claimed is:

1. A direct plasma polymerization process for making a durably wettable, liquid pervious web for use as a topsheet in an absorbent article, the process comprising:
 - (i) introducing a web to a plasma reaction zone; and
 - (ii) coating at least one of the surfaces of the web with a coating of polymerized monomers, wherein the coating is less than 2.5 microns thick and is derived from a monomer gas stream that will provide a hydrophilic coating upon plasma polymerization;said process characterized in that the web is selected from the group consisting of polymeric films, apertured polymeric films, nonwovens and apertured nonwovens; wherein the polymerized monomers cause at least one surface of the web to become durably-wettable.
2. The process of Claim 1 wherein at least one surface of the durably-wettable, liquid pervious web has a Post Aging contact angle that is not more than 60 degrees greater than the Pre Aging contact angle, preferably not more than 40 degrees greater than the Pre Aging contact angle and most preferably not more than 20 degrees greater than the Pre Aging contact angle.
3. The process of any preceding claim wherein at least one surface of the durably-wettable, liquid pervious web has a Post Washing contact angle that is not more than 60 degrees greater than the Pre Washing contact angle, preferably is not more than 40 degrees greater than the Pre Washing contact angle and most preferably not more than 20 degrees greater than the Pre Washing contact angle.
4. The process of any preceding claim wherein the process further comprises the step of cleaning the surface of the web by exposing the surface to plasma conditions or an energy source selected from the group consisting of infra red, electron beam, thermionic or ultra violet radiation and mixtures thereof, prior to introduction of the monomer gas stream of step (ii).
5. The process of Claim 4 wherein the step of cleaning the surface of the web by exposing the web to plasma conditions comprises introduction of a gas stream comprising a material selected from the group consisting of Ar, O₂, and mixtures thereof.
6. The process of any preceding claim wherein the process comprises the step of further modifying the hydrophilic surface by introducing the web formed in step (ii) to a surface modifying gas stream, the gas stream comprising N₂O and CO₂; or an energy source selected from the group consisting of infra red, electron beam, thermionic or ultra violet radiation and mixtures thereof.

7. The process of any preceding claim further comprising a final step comprising aperturing the coated web.
8. The process of any preceding claim wherein the polymeric film is derived from a material selected from the group consisting of polyolefins, polyesters, and mixtures thereof.
9. The process of Claim 8 wherein the polymeric film is derived from a material selected from the group consisting of polyethylene, polypropylene, poly(1-butene), poly(2-butene), poly(1-pentene), poly(2-pentene), poly(3-methyl-1-pentene), poly(4-methyl-1-pentene), 1,2-poly-1,3-butadiene, 1,4-poly-1,3-butadiene, polyisoprene, blends thereof, random copolymers thereof, and block copolymers thereof.
10. The process of any preceding claim wherein the monomer gas stream comprises a monomer selected from the group consisting of (i) silanes of the formula $\text{Si}(\text{R})_4$ where each R is the same or different and is selected from H; a $\text{C}_1\text{-C}_8$ linear or branched alkyl or alkoxy; a $\text{C}_6\text{-C}_{10}$ aryl, unsubstituted or substituted with $\text{C}_1\text{-C}_4$ linear or branched alkyl; a vinyl radical; or a $\text{C}_3\text{-C}_5$ allyl radical; provided not more than two R groups are H; (ii) organosilicones of the formula $\text{R}'\text{R}''\text{R}'''\text{Si}[-\text{O}-\text{Si}(\text{R}')(\text{R}'')-]_n-\text{R}'''$, where R' , R'' and R''' can be the same or different and are $\text{C}_1\text{-C}_8$ linear or branched alkyl or alkoxy, wherein R' and R'' may be hydrogen provided that no more than 50% of the R' and R'' groups are hydrogen, and n is 1, 2 or 3; and (iii) mixtures thereof; and wherein said monomer gas stream further comprises oxygen when said monomer of said gas stream consists only of said silanes.
11. The process of Claim 10 wherein the monomer gas stream comprises a monomer selected from the group consisting hexamethyldisiloxane, methyltrimethoxy silane, vinyltrimethoxy silane, vinyltriethoxy silane and oxygen, ethylmethoxy silane, ethyltrimethoxy silane, tetraethoxy silane, cyclohexylmethyl-dimethoxy silane, dicyclopentyl-dimethoxy silane, phenyltriethoxy silane, diphenyldimethoxy silane, tetramethyldisiloxane, hexamethyltrisiloxane, and mixtures thereof; and wherein said monomer gas stream further comprises oxygen when said monomer of said gas stream consists only of said silanes.
12. The process of any preceding claim wherein the gas of the monomer gas stream is ionized via pulsation of high frequency microwaves or radiowaves.
13. An absorbent article characterized in that said absorbent article comprises a durably wettable, liquid pervious topsheet produced by the processes of anyone of the preceding claims.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/21709

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B05D7/24 D06M10/02 D06M10/08 D06M10/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B05D D06M A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YOSHIMURA K ET AL: "PREPARATION OF HYDROPHILIC PLASMA-POLYMERS DERIVED FROM OXYGEN- CONTAINING ORGANIC MONOMERS" JOURNAL OF APPLIED POLYMER SCIENCE, US, JOHN WILEY AND SONS INC. NEW YORK, vol. 59, no. 6, 7 February 1996 (1996-02-07), pages 1033-1042, XP000551855 ISSN: 0021-8995 page 1034, left-hand column, line 12 - line 20 — —/—	1, 8, 12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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Date of the actual completion of the international search

14 February 2000

Date of mailing of the international search report

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Brothier, J-A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/21709

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 198931 Derwent Publications Ltd., London, GB; Class A35, AN 1989-224504 XP002130415 & JP 01 161026 A (TAKAMATSU YUSHI KK), 23 June 1989 (1989-06-23) abstract</p>	1,6,8
X	<p>DATABASE WPI Section Ch, Week 199338 Derwent Publications Ltd., London, GB; Class A35, AN 1993-297840 XP002130416 & JP 05 209072 A (JAPAN SYNTHETIC RUBBER CO LTD), 20 August 1993 (1993-08-20) abstract</p>	1,2,12
X	<p>DATABASE WPI Section Ch, Week 198650 Derwent Publications Ltd., London, GB; Class A14, AN 1986-329479 XP002130417 & JP 61 246204 A (TOKAI PULP KK), 1 November 1986 (1986-11-01) abstract</p>	1
P,X	<p>WO 99 05358 A (SAYERS IAN CHRISTISON ;SCAPA GROUP PLC (GB)) 4 February 1999 (1999-02-04) the whole document</p>	1,10
P,X	<p>WO 99 39842 A (MOSER EVA MARIA ;EMPA ST GALLEN EIDGENOESSISCHE (CH)) 12 August 1999 (1999-08-12) the whole document</p>	1,8
P,X	<p>EP 0 896 035 A (UNIV TEXAS) 10 February 1999 (1999-02-10) the whole document</p>	1
A	<p>WO 95 04609 A (CIBA GEIGY AG ;KLING RENATE & LF (DE); SEIFERLING BERNHARD (DE); B) 16 February 1995 (1995-02-16) page 15</p>	3
A	<p>US 5 529 631 A (FUKUURA YUKIO ET AL) 25 June 1996 (1996-06-25) the whole document</p>	1
	-/-	

INTERNATIONAL SEARCH REPORT

Intern. Application No.

PCT/US 99/21709

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LEE S H ET AL: "PREPARATION AND CHARACTERIZATION OF THIN FILMS BY PLASMA POLYMERIZATION OF HEXAMETHYLDISILOXANE" THIN SOLID FILMS, CH, ELSEVIER-SEQUOIA S.A. LAUSANNE, vol. 325, no. 1/02, 18 July 1998 (1998-07-18), pages 83-86, XP000667948 ISSN: 0040-6090 the whole document _____	10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/21709

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 1161026 A	23-06-1989	NONE	
JP 5209072 A	20-08-1993	NONE	
JP 61246204 A	01-11-1986	NONE	
WO 9905358 A	04-02-1999	AU 8452698 A	16-02-1999
WO 9939842 A	12-08-1999	AU 2147299 A	23-08-1999
EP 0896035 A	10-02-1999	AU 7844098 A	18-02-1999
		CN 1213661 A	14-04-1999
		JP 11181330 A	06-07-1999
WO 9504609 A	16-02-1995	AT 174538 T	15-01-1999
		AU 693111 B	25-06-1998
		AU 7609794 A	28-02-1995
		DE 69415323 D	28-01-1999
		DE 69415323 T	24-06-1999
		EP 0713429 A	29-05-1996
		ES 2124908 T	16-02-1999
		FI 960528 A	05-02-1996
		JP 9501705 T	18-02-1997
		NO 960516 A	08-02-1996
		NZ 271971 A	25-09-1996
		ZA 9405929 A	20-03-1995
US 5529631 A	25-06-1996	JP 2811820 B	15-10-1998
		JP 3143930 A	19-06-1991

4

UU	UU	SSSS	3333	3333	666	444	3333	777777
UU	UU	SS SS	33 33	33 33	66	4444	33 33	77 77
UU	UU	SSS	33	33	66	44 44	33	77
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US005224441A

United States Patent [19][11] **Patent Number:** **5,224,441****Felts et al.**[45] **Date of Patent:** **Jul. 6, 1993****[54] APPARATUS FOR RAPID PLASMA TREATMENTS AND METHOD**

[75] Inventors: John T. Felts, Alameda; Hood Chatham, III, Fairfield; Joseph Countrywood, Napa; Robert J. Nelson, Walnut Creek, all of Calif.

[73] Assignee: The BOC Group, Inc., New Providence, N.J.

[21] Appl. No.: 767,146

[22] Filed: Sep. 27, 1991

[51] Int. Cl.³ C23C 16/50

[52] U.S. Cl. 118/718; 118/723; 118/724; 118/730; 422/186.05

[58] Field of Search 118/718, 723, 730; 156/345; 422/186.04, 186.05, 186.06; 315/111.21, 111.41, 111.71

[56] References Cited**U.S. PATENT DOCUMENTS**

3,898,952 8/1975 Shirahata et al. 118/723 X
4,277,516 7/1981 Behn et al. 118/718 X
4,384,918 5/1983 Abe 156/643
4,400,410 8/1983 Green et al. 427/569 X
4,551,310 11/1985 Imada et al. 422/186.05
4,557,946 12/1985 Sacher et al. 427/41
4,559,112 12/1985 Tamamura et al. 204/12
4,599,678 7/1986 Wertheimer et al. 361/323
4,741,801 5/1988 Coleman 156/643
4,842,707 6/1989 Kinoshita 118/723 X
4,847,469 7/1989 Hofmann et al. 219/273
4,863,756 9/1989 Hartig et al. 427/39
4,920,917 5/1990 Nakatani et al. 118/723 X
4,960,073 10/1990 Suzuki et al. 118/723
4,968,918 11/1990 Kondo et al. 315/111.21
4,986,890 1/1991 Setoyama et al. 204/298.06
4,991,542 2/1991 Kohmura et al. 118/723

4,997,519 3/1991 Kondo et al. 156/643
5,009,738 4/1991 Gruenwald et al. 156/345
5,013,416 5/1991 Murayama et al. 204/192.1
5,041,304 8/1991 Kusano et al. 427/569 X

FOREIGN PATENT DOCUMENTS

0107510A2 5/1984 European Pat. Off. .
0198604A1 10/1986 European Pat. Off. .
0248274 12/1987 European Pat. Off. 118/718
0299754A2 1/1989 European Pat. Off. .
0406691A2 1/1991 European Pat. Off. .
0084516 5/1984 Japan 118/718
0124038 7/1984 Japan 118/718
59-213735 12/1984 Japan .
60-226533 11/1985 Japan .
61-207445 9/1986 Japan .
02-281420 11/1990 Japan .
02267267 11/1990 Japan 118/718
03183782 8/1991 Japan 118/718
WO91/17561 11/1991 PCT Int'l Appl. .

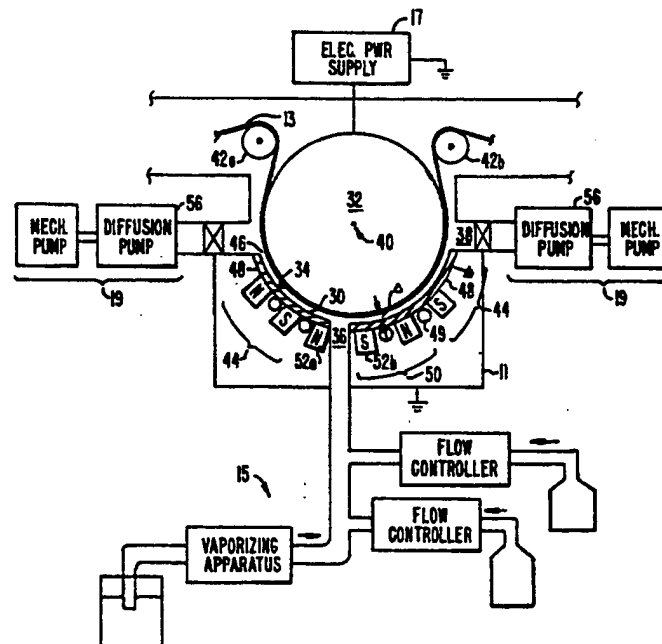
Primary Examiner—Brian E. Hearn

Assistant Examiner—Jonathan D. Baskin

Attorney, Agent, or Firm—David A. Draegert; Larry R. Cassett

[57]**ABSTRACT**

A plasma treating apparatus is useful for coating substrates with thin films having vapor barrier properties at relatively rapid deposition rates. The apparatus comprises an evacuable chamber, an electrically powered electrode defining a plasma-facing surface within the chamber, and a shield spaced a distance Δ transverse to the plasma-facing surface. During plasma treatments, the plasma is confined to within distance Δ while a substrate is continuously fed through the confined plasma.

19 Claims, 1 Drawing Sheet

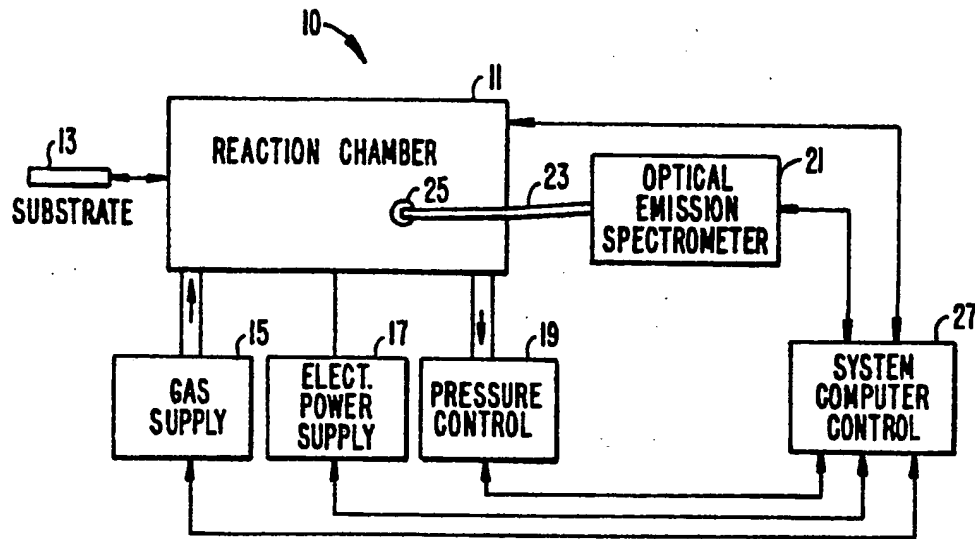


FIG. 1.

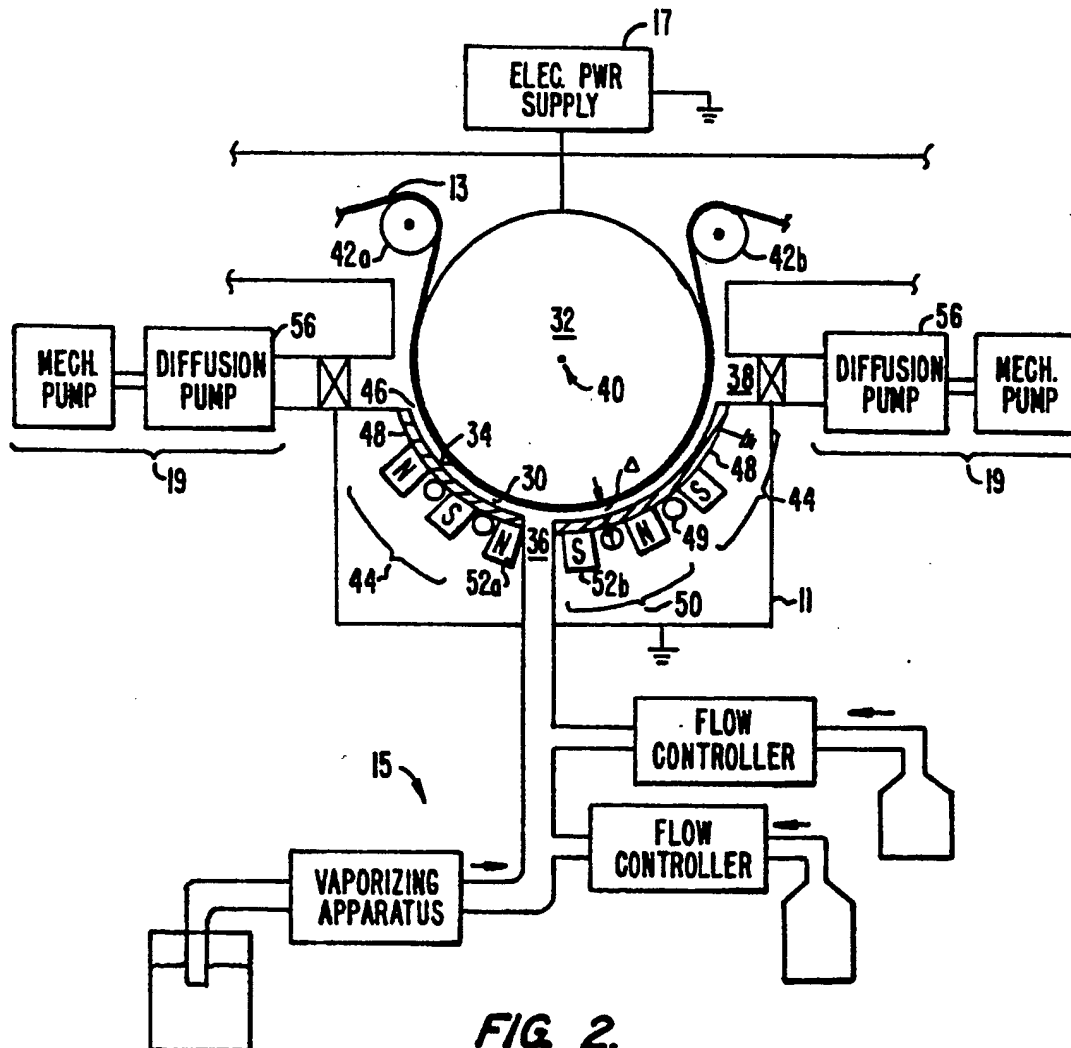


FIG. 2.

APPARATUS FOR RAPID PLASMA TREATMENTS AND METHOD

FIELD OF THE INVENTION

The present invention relates to the plasma treatments of substrates, and more particularly to the rapid plasma enhanced deposition of silicon oxide based thin films on substrates to provide gas transmission barriers useful for packaging applications.

BACKGROUND OF THE INVENTION

Plasma polymerization, sometimes designated "plasma enhanced chemical vapor deposition," or "PECVD," has been a known technique to form films on various substrates. For example, mixtures of silane with or without oxygen, nitrous oxide or ammonia have been plasma polymerized to form silicon oxide films. Sacher et al., U.S. Pat. No. 4,557,946, issued Dec. 10, 1985 describes use of plasma polymerized coatings from organosilicon compounds to form a moisture barrier on the substrate by heating the substrate and controlling the plasma power level. Wertheimer et al., U.S. Pat. No. 4,599,678, issued Jul. 8, 1986, discloses use of an organosilicon in a glow discharge to coat thin film capacitors when these substrates are heated to a temperature in excess of 50° C.

In general, the films formed from organo-silicons have typically been formed at a relatively low deposition rate (as compared with, for example, magnetron sputtering), have tended to be soft, and often have been hazy. The requirement that the substrate be heated, as in Sacher et al. and Wertheimer et al., is also disadvantageous for some substrates.

A further problem with use of organosilicon compounds in plasma enhanced deposition has been the variation in polymerization conditions and lack of control during the deposition. The traditional method used to control plasma processes has been the use of power, pressure and flow to monitor and attempt to control the process. However, these three variables represent inputs and do not accordingly control the thin films being produced. As a consequence, the scale-up of such a process is extremely complex.

In early microelectronic PECVD reactors, the plasma was generated between two parallel, circular electrodes. The wafers were loaded onto the lower, electrically grounded, electrode. The upper electrode was connected to a rf generator through an impedance matching network. The reactants were fed in from a gas ring, entered the plasma region (i.e., the region between the electrodes) at its outer edge, and flowed radially inward toward a pumping port at the center of the electrode. These reactors have commonly been known as "radial flow" reactors.

In "inverse" radial flow reactors, the gas inlet has been at the center of the lower electrode, with the gas flow directed radially outward. A magnetic drive assembly permitted rotation of the lower electrode, thus randomizing the substrate position and optimizing deposition uniformity.

In hot-wall, batch PECVD systems, the deposition chamber consisted of a quartz tube placed within a resistively heated furnace. Vertically oriented graphite slabs carried the wafers in slots. Every other slab was connected to the same rf power terminal and a glow discharge was generated between adjacent electrodes.

The reactants were directed along the axis of the chamber tube and between the electrodes.

More recently, PECVD has been employed to coat large substrates, e.g., plastic containers and long rolls of flexible films for food packaging applications. In the process described by Ser. No. 07/426,514, filed Oct. 24, 1989, of common assignment herewith, plasma polymerization is used to deposit silicon oxide based thin films from volatile organosilicon compounds. This method of depositing an adherent, hard silicon oxide based film comprises providing a gas stream with several components, establishing a glow discharge plasma derived from the gas stream, or one of its components, in a previously evacuated chamber with a substrate removably positioned in the plasma, and controllably flowing the gas stream into the plasma to deposit a silicon oxide onto the substrate when positioned in the plasma. The gas stream components include a volatilized organosilicon compound, oxygen, and an inert gas such as helium or argon.

The gas stream is controllably flowed into the plasma by volatilizing the organosilicon exterior to the chamber and admixing metered amounts of organosilicon with oxygen and the inert gas. Controlling the flowing gas stream into the plasma preferably includes adjusting the amount of organosilicon entering the chamber during the deposition. Control can be achieved with use of the flow vaporizer described by U.S. Pat. No. 4,847,469, issued Jul. 11, 1989, inventors Hofmann et al.

Films with reduced permeability to vapors such as water, oxygen, and carbon dioxide are useful for a variety of applications, one of which is to package foods. Such films are typically composites of materials. For example, one layer is often a flexible polymer, such as a polyethylene or polypropylene, while another layer is coated on or coextruded with the one layer and serves as a barrier layer. Barrier layers can generally be viewed as substantially organic based or substantially inorganic based.

Plasma assisted or enhanced processes, in addition to coating applications such as above described, include plasma etching or cleaning where substrate surfaces are modified. Plasma etching, for example, is used in manufacturing integrated electronic circuits.

A variety of equipment for plasma treatments are known. U.S. Pat. No. 4,863,756, issued Sep. 5, 1989, inventors Hartig et al., describes plasma coating equipment that includes magnets disposed to one side of an electrode while the other electrode side holds the substrate being coated, which faces a plasma.

U.S. Pat. No. 4,968,918, issued Nov. 6, 1990, inventors Kondo et al., discloses a plasma treating apparatus having a plurality of powered electrodes. The substrate being plasma treated is passed proximate to the powered electrodes.

U.S. Pat. No. 5,009,738, issued Apr. 23, 1991, inventor Gruenwald, discloses a plasma etching apparatus in which the substrate being treated is pressed against a cathode and the apparatus is said to achieve an improved heat elimination for the substrate during the etching process.

U.S. Pat. No. 5,013,416, issued May 7, 1991, inventor Murayama, discloses an apparatus for manufacturing transparent, conductive film by using an ion-plating method with a pressure-gradient plasma gun and intermediate electrodes for plasma control. The apparatus is said to permit manufacture of conductive films at high substrate velocity.

IN THE DRAWINGS

FIG. 1 is a general schematic diagram illustrating a plasma vacuum system with which embodiments of the invention can be used; and

FIG. 2 schematically illustrates a side sectional view of the reaction chamber and its associated equipment utilizing various aspects of the present invention.

SUMMARY OF THE INVENTION

It is one object of this invention to provide an apparatus in which one can reproducibly deposit adherent, hard silicon oxide based thin films at commercially feasible, relatively rapid deposition rates on small or large substrates, preferably with preselected gas barrier properties.

In one aspect of the invention, a plasma treating apparatus comprises an evacuable chamber, means for forming a plasma within the chamber, an electrically powered electrode defining a plasma-facing surface within the chamber, means for communicating electricity from the electrode to a substrate and for exposing a continuously changeable portion of the substrate to plasma, and means for confining the plasma adjacent to the continuously changeable substrate portion being treated. The confining means confines the plasma at the substrate portion being plasma treated to within a distance Δ in combination with the apparatus elements, for achieving relatively rapid depositions of films that provide gas barrier properties. The confining means forms a ground plane with respect to the negatively biased electrode.

In another aspect of the present invention, a silicon oxide based film is deposited having vapor barrier properties. Practice of the invention permits preparation of particularly preferred flexible polymer-substrate embodiments coated to have a permeability to oxygen gas that is less than about 0.1 cc/100 in²/day with thin film thicknesses less than about 1000 Å at deposition rates greater than about 250 Å/sec. Such embodiments are useful where inert, flexible packaging with excellent vapor and gas barrier properties are required, such as for serum and blood bags in medical applications and for food packaging of very oxygen-sensitive foods, at commercial coating rates.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The inventive plasma treating apparatus is useful in coating applications, as well as plasma etching or cleaning where substrate surfaces are to be modified. The best mode contemplated for using the inventive plasma treating apparatus is where the substrate to be plasma treated is flexible. Flexibility of substrate being treated is due to the preferred configuration of the system that carries the substrate through the plasma during plasma treatment. This will be more fully discussed hereinafter.

Various flexible plastics, whether electrically conducting, semi-conducting, or non-conducting are suitable and may be coated in accordance with the invention. For example, various flexible plastics such as poly(ethyleneterephthalate) (PET) or polycarbonate (PC) resins, useful for packaging foods, may be coated in accordance with the invention to retard oxygen, carbon dioxide or moisture permeation. Although thicknesses of flexible substrates will be up to about 10 mils, the thicknesses are usually about 0.5–1 mil for food packaging applications.

The inventive apparatus is preferably used to prepare flexible films with reduced permeability to vapors such as water, oxygen, and carbon dioxide. It has been discovered, as described in Ser. No. 07/562,119, filed Aug. 3, 1990, of common assignment herewith, that gas transmission properties are a function of film thickness on flexible substrates and surprisingly have an optimal range of thickness to provide the maximal barrier properties, with both thicker and thinner films outside the optimal range having less desirable barrier properties. Articles prepared in accordance with the invention preferably are where a polymer substrate and thin film carried on the substrate together have a permeability to oxygen gas that is less than about 0.1 cc/100 in²/day and the thin film has a thickness less than about 1000 Å, more preferably less than about 600 Å, most preferably the thin film has a thickness between about 100 Å to about 400 Å and the coated plastic film has an oxygen permeability of less than about 0.04 cc/100 in²/day.

In one embodiment of the invention, a silicon oxide based film with vapor barrier properties is deposited from a glow discharge plasma derived from a gas stream including a volatilized organosilicon compound, oxygen, and an inert gas. Although the preferred process has an organosilicon compound as a starting material, the films therefrom are substantially inorganic as evidenced by bonding analysis. However, films that are silicone in nature may be prepared if desired, as further described hereinafter. The typical, substantially inorganic silicon oxide based films deposited in accordance with the invention are characterized by a high degree of crosslinking (determined by Fourier transform infrared spectroscopy, or FTIR). Gas stream control for such an embodiment is preferably by means of plasma diagnostics, as described by U.S. Pat. No. 4,888,199, issued Dec. 19, 1989, inventors Felts and Lopata.

The combination of oxygen component and inert gas component with the volatilized organosilicon component has been found greatly to increase the hardness property of thin films. Films prepared either with the organosilicon combined only with oxygen or the organosilicon combined only with an inert gas such as helium or argon had a hardness measured by the ASTM D3363-74 (standard test method for film hardness) pencil test of only 2 or 3. By contrast, films made with a combination of organosilicon, oxygen, and inert gas in accordance with the invention have hardnesses by this test of about 7 to about 9+. The numbers reported are based on a scale of 0 to 10 where 0 means the least scratch resistance, while 10 means there was no damage to the coating when abraded in accordance with ASTM D3363-74. Accordingly, thin films can be prepared that are typically harder by a factor of 2 or 3 with respect to films deposited with the volatilized organosilicon component in combination with either oxygen or inert gas.

Suitable organosilicon compounds for the gas stream are liquid at about ambient temperature, and when volatilized have a boiling point above about ambient temperature. These include methylsilane, dimethylsilane, trimethylsilane, diethylsilane, propylsilane, phenylsilane, hexamethyldisilane, 1,1,2,2-tetramethyldisilane, bis(trimethylsilyl) methane, bis(dimethylsilyl) methane, hexamethyldisiloxane, vinyl trimethoxy silane, vinyl triethoxy silane, ethylmethoxy silane, ethyltrimethoxy silane, divinyltetramethyldisiloxane, divinylhexamethyltrisiloxane, and trivinylpentamethyl-trisiloxane.

Among the preferred organosilicons are 1,1,3,3-tetramethyldisiloxane, hexamethyldisiloxane, vinyltri-

thylsilane, methyltrimethoxysilane, vinyltrimethoxysilane and hexamethyldisilazane. These preferred organosilicon compounds have boiling points of 71° C., 101° C., 55.5° C., 102° C., 123° C., and 127° C., respectively.

The volatilized organosilicon component is preferably admixed with the oxygen component and the inert gas component before being flowed into the chamber. The quantities of these gases being so admixed are controlled by flow controllers so as to adjustably control the flow rate ratio of the gas stream components.

The organosilicon compound and oxygen of the gas stream during the depositing may be, for example, in a flow rate ratio of about 0.1:1.0 and the inert gas of the gas stream preferably is helium or argon, more preferable is helium. When the inert gas is helium or argon, then a suitable flow rate ratio of organosilicon compound, oxygen and inert gas is about 0.1:1.0:1.0. Other flow rate ratios may be used, however, if desirable.

In addition to organosilicon, oxygen and inert gas in the gas stream, minor amounts (not greater than about 1:1 with respect to the organosilicon, more preferably about 0.4 to 0.1:1 with respect to the organosilicon) of one or more additional compounds in gaseous form may be included for particular desired properties. For example, inclusion of a lower hydrocarbon such as propylene improves many frequently desired properties of the deposited films (except for light transmission), and bonding analysis indicates the film to be silicon dioxide in nature. Use of methane or acetylene, however, produces films that are silicone in nature. The inclusion of a minor amount of gaseous nitrogen to the gas stream increases the deposition rate, improves the transmission and reflection optical properties on glass, and varies the index of refraction in response to varied amounts of N₂. The addition of nitrous oxide to the gas stream increases the deposition rate and improves the optical properties, but tends to decrease the film hardness. A particularly preferred gas stream composition has 500 to 1,000 SCCM organosilicon, 3,000 to 8,000 SCCM O₂, and 3,000 to 5,000 SCCM He.

Although the inventive apparatus that will now be more specifically described with reference to FIGS. 1 and 2 is preferably used to reproducibly deposit adherent, hard silicon oxide based thin films from a plasma that is derived from a gas stream including organosilicon, oxygen, and inert gas, one can also use the inventive apparatus for plasma etching or cleaning or non-SiO_x chemistry.

Turning to FIG. 1, a plasma treating apparatus 10 embodiment is schematically illustrated that includes an enclosed chamber 11 in which a plasma is formed and in which a substrate, such as substrate 13, is continuously introduced for plasma treating. One or more gases are supplied to the chamber 11 by a gas supply system 15. Where, for example, one wishes to prepare articles with vapor barrier properties, then gas supply system 15 can supply the oxygen component, inert gas component and volatilized organosilicon component. However, if one wishes to plasma etch, for example, then gas supply system 15 can supply oxygen, or oxygen and helium, or a suitable etchant gas mixture (e.g., oxygen and a halogen component).

An electric field within chamber 11 is created by a power supply 17. Power supply 17 typically provides about 8 kW during plasma treatments such as vapor barrier coating. Chamber 11 is evacuable, and a low pressure is maintained by a pumping and pressure control system 19. Chamber 11 and the pumps/pressure

control system 19 should be capable of maintaining a pressure of less than about 0.1 torr during plasma treatment, and more preferably 0.05 torr.

An optical emission spectrometer 21 is preferably connected through an optical fiber light transmission medium 23 to the chamber 11 in some appropriate manner to couple the visible and near visible (especially the ultraviolet range) emission of the plasma to the spectrometer. A quartz window 25 in a sidewall of the reaction chamber can be used to optically couple the plasma emission with the exterior fiber medium 23. A general system control 27, including a computer controlled portion, is connected to each of the other components of the system in a manner to receive information from them and to send controlling commands to them. Control of coating processes through use of readings from spectrometer 21 is more fully described by U.S. Pat. No. 4,888,199, incorporated by reference.

A more detailed explanation of chamber 11 will now be given with respect to FIG. 2 (where a PECVD, or plasma polymerization, process as the plasma treatment is exemplified).

Chamber 11 includes means 30 for forming a plasma within chamber 11. The plasma forming means 30 includes an electrically powered electrode 32 defining a plasma-facing surface 34 within chamber 11. Plasma forming means 30 in the embodiment illustrated by FIG. 2 also includes a source of film-forming gas, such as the gas supply system 15 with gas inlet 36.

Substrate 13 is continuously fed into, through, and out of chamber 11 as a strip, or web, with a continuously changeable portion of substrate 13 being exposed to the plasma so as to be plasma treated, such as coated with a thin film having vapor barrier properties. While a continuously changeable portion of substrate 13 is being plasma treated, substrate 13 is also negatively biased. These two functions are achieved by a means 38 for communicating electricity from electrode 32 to substrate 13 when within chamber 11 and for exposing a continuously changeable portion of the substrate to the plasma during plasma treatment. Negative bias assists in focusing the deposition onto the substrate and permits deposition with lower power settings. However, when the substrate is conductive, then one can bias substantially directly (that is, without a separate electrode).

One embodiment of communicating and exposing means 38 is wherein electrode 32, or at least its plasma-facing surface 34, is cylindrical, or drum-like, although generally arcuate configurations that extend along an axis 40 can be used. The purpose of such an arcuate, or cylindrical, configuration for plasma-facing surface 34 is so that a flexible substrate 13 can be placed into rolling contact with the plasma-facing surface 34 and thus fed as a web, such as with the assistance of secondary rollers 42a, 42b which can be adjusted to tension substrate 13 when fed through the plasma while a negative bias is imposed upon at least that portion of the substrate being exposed to the plasma at any one point in time during the plasma treatment. The substrate portion is within a confined plasma because a means 44 confines the plasma to a band 46 having a dimension, or width, as distance Δ. Distance Δ extends transversely to plasma-facing surface 34 and axis 40. As will be discussed and exemplified hereinafter in more detail, the plasma confinement is crucial for achieving high utilization of the process gas and power with resultant high deposition rates. Confining means 44 thus confines the plasma to

the continuously changeable portion of substrate 13 and to within distance Δ outward (radially outward when surface 34 is cylindrical) from the substrate. Distance Δ should be not greater than about 12 inches, more preferably be not greater than about 4 inches, more preferably is in a range of about 2 inches to about 3 inches. Distance Δ preferably is not less than about 0.5 inch because otherwise the plasma will tend to be extinguished.

Confining means 44 preferably includes a shield 48 that is mounted in chamber 11 so as to be spaced the distance Δ from the plasma-facing surface 34. Where plasma-facing surface 34 is cylindrical, then shield 48 will be coaxial therewith, and the length of its arc (thus defining the length of plasma band 46) is preferably about 70% of the cylindrical drum surface (that is, an arc of approximately 250°), but should be at least an appreciable arc length in order to allow high speed plasma treating of the flexible substrate material.

Shield 48 is preferably cooled, such as by various cooling means known to the art and generally illustrated by cooling tubing 49. Shield 48 should be electrically grounded and thus establishes a "ground plane" (that is, a return path for the power supply). It is believed preferable to form shield 48 as part of a chamber 11 wall with the pressure within the shield 48 (defined by distance Δ and the arc length for shield 48) being greater than the surrounding chamber 11 space, which is evacuated at about 1 micron or less.

Confining means 44 preferably further comprises magnetic means 50 for generating a magnetic field within the plasma. Magnetic means 50 may be at least one magnetic pole pair 52a, 52b positioned adjacent to shield 48, such as by being mounted on shield 48 on the shield side obverse with respect to the shield side facing the plasma. A plurality of magnetic pairs are preferred with alternating pole configuration around the entire shield 48. As illustrated in FIG. 2, cooling lines 49 are preferably interposed between such alternating magnetic pole pairs. As exemplified by the FIG. 2 embodiment, the gas inlet 36 is symmetrically disposed with respect to the arc length of shield 48 and pumps 56 are preferably positioned symmetrically at each open end of shield 48.

The inventive apparatus 10 embodiment as has been described will now be further exemplified by reference to the preparation of a substrate with vapor barrier properties using an inventive apparatus in Example 1, and Example 2 also exemplifies distance Δ experiments.

Example 1 illustrates practice of the substrate preparation method through use of the inventive apparatus. 50

EXAMPLE 1

A gas mixture of four-tenths of a standard liter per minute (SLM) of 1,1,3,3-tetramethyldisiloxane (TMDSO), five SLM of oxygen and four SLM of helium was introduced to the process chamber by a linear gas manifold. The vacuum pumping was adjusted to yield a process zone pressure near 45 millitorr. The capstan tensions of the rollers were set at about 17 pounds and the rewind and unwind tensions were set at about 10 pounds. The linespeed of the PET web was established at 100 feet per minute. The drum was electrically powered with four kilowatts at a frequency of 50 kilohertz. The pumping was then tuned to obtain a process pressure of 60 millitorr. A liquid with high thermal conductivity and extremely low electrical conductivity was chilled and circulated through the drum, so as to keep the drum temperature at 20° C. The plasma

confinement shield was water cooled to 40° C., and had ten magnet bars arranged at regularly spaced intervals parallel to the axis of the powered drum. The magnetic field along each magnet bar faced the same direction, while from magnet bar to magnet bar the magnetic field was reversed 180 degrees, resulting in a multipole arrangement. The length (arc) of the deposition zone was 27 inches.

The substrate Was PET of 12 μ m thickness coated as described above with a silicon oxide based coating, which resulted in a mean oxygen transmission rate of 1.5 cc/m² deviation of 0.2 cc/m²/day for cc/m²/day (with a standard deviation of 0.2 cc/m²/day for five samples). The film thickness was about 30 nm with a composition determined to be about 33% silicon and 67% oxygen.

EXAMPLE 2

A statistically designed experiment was performed to determine an optimum distance Δ . In this designed experiment, the TMDSO flow was varied from 0.74 to 0.52 SLM, the oxygen flow from 5 to 3 SLM, the power from 6 to 5 kW, and the distance Δ from 3 to 1 inch. In this range of variables, the distance Δ and the TMDSO flow were the variables which had the most significant effects on the oxygen gas transmission rate. Furthermore, in this range of variables, the results suggest that the smaller separation Δ yields a lower oxygen transmission rate. Current commercial manufacturing mechanical limitations typically allow for a minimum Δ of about two inches, which was the spacing used in Example 1 above.

It is to be understood that while the invention has been described above in conjunction with preferred specific embodiments, the description and examples are intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims.

What is claimed is:

1. A plasma treating apparatus comprising:

an evacuable chamber;

means for forming a plasma within the chamber, the plasma forming means including an electrically powered electrode defining a plasma-facing surface within the chamber;

means for communicating electricity from the electrode to a substrate when the substrate is within the chamber by placing the plasma-facing surface into rolling contact with the substrate and for exposing a continuously changeable portion of the substrate to plasma during plasma treatment; and,

means for confining the plasma adjacent to the continuously changeable substrate portion, the confining means including a grounded shield.

2. The apparatus as in claim 1 wherein the electrically powered electrode is negatively biased with respect to the confining means.

3. The apparatus as in claim 1 wherein the confining means confines the plasma at the changeable substrate portion and to within a distance Δ between about 0.5 inch to about 12 inches outwardly therefrom.

4. The apparatus as in claim 3 wherein the grounded shield is cooled, spaced at least Δ from the changeable substrate portion and the plasma is substantially confined between the changeable substrate portion and the shield.

5. The apparatus as in claim 4 wherein the plasma-facing surface is arcuate and longitudinally extends along an axis, and the shield is coaxial therewith.

6. The apparatus as in claim 4 wherein the confining means includes magnetic means for generating a magnetic field extending into the plasma and intersection the plasma-facing surface.

7. The apparatus as in claim 7 wherein the magnetic means includes at least one magnetic pole pair positioned adjacent to the shield.

8. The apparatus as in claim 4 wherein the chamber is adapted to be maintained at less than about 0.1 torr during plasma treatment of the substrate.

9. The apparatus as in claim 8 wherein the plasma forming means includes a source of film-forming gas, the gas being capable of forming an adherent substrate coating during plasma treatment of the substrate.

10. The apparatus as in claim 9 wherein the plasma forming means includes an inlet associated with the grounded shield for introducing a film-forming gas stream from the source thereof into the distance Δ .

11. The apparatus as in claim 1 wherein the plasma-facing surface is cylindrical.

12. The apparatus as in claim 11 wherein the substrate is substantially electrically non-conductive and flexible.

13. The apparatus as in claim 1 wherein the substrate is substantially electrically conductive and the plasma-facing surface is formed by the substrate.

14. A thin film coating apparatus comprising:
a chamber evacuable to less than about 0.1 torr;

means for forming a plasma within the chamber from a film-forming gas stream, the film forming gas stream capable of depositing an adherent coating onto a substrate;

means for confining the plasma to a continuously changeable portion of a substrate being fed through the chamber during coating thereof and to within a distance Δ outward therefrom, the confining means including a grounded shield; and

means for negatively biasing the substrate portion being coated with respect to the chamber and with respect to the grounded shield.

15. The coating apparatus as in claim 14 wherein the distance Δ is between about two inches to about four inches.

16. The coating apparatus as in claim 14 wherein the grounded shield is cooled and is spaced at least the distance Δ from the changeable substrate portion.

17. The coating apparatus as in claim 16 wherein the plasma-facing surface is arcuate and longitudinally extends along an axis, and the shield is coaxial therewith.

18. The coating apparatus as in claim 17 wherein the magnetic means includes at least one magnetic pole pair positioned adjacent to the shield.

19. The coating apparatus as in claim 14 wherein the negative biasing means includes an electrode defining a plasma-facing surface within the chamber, and the changeable substrate portions are rollingly contacted therewith during coating.

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